Design and Synthesis of Thermally Curable Polymers with Benzoxazine Functionalities

*Baris Kiskan, Burcin Gacal, M. Atilla Tasdelen, Demet Colak, Yusuf Yagci**

Summary: In this paper, synthetic strategies for the preparation of structurally different polymers, namely polystyrene (PSt), poly(ε-caprolactone) (PCL), poly(propyleneoxide) (PPO), poly(methyl methacrylate) (PMMA), and poly(styrene-*alt*-maleimide) (PSt-*alt*-MI) with thermally curable benzoxazine groups have been outlined. Specifically, these groups were incorporated into PSt and PCL by using two controlled polymerization methods, namely Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP), respectively. Modification of linear and branched poly(propylene amine)s via Mannich reaction yields the corresponding benzoxazine functional PPOs. The photoinitiated polymerization of olefinic monomers such as methyl methacrylate by using benzoxazines as hydrogen donor in conjunction with aromatic carbonyl compounds is another suitable method for the desired functionalization. Moreover, benzoxazine substituted maleimide was copolymerized with styrene to yield perfectly alternating benzoxazine functional copolymers (PSt-*alt*-MI).

Keywords: high performance polymers; phenolic resins; polybenzoxazine; thermal curing

Introduction

Among various high performance materials, polybenzoxazine,[1–4] as a recently developed thermosetting phenolic resin, has received much interest for its unique characteristics such as heat resistance, good flame retardance, low moisture absorption, good mechanical properties and excellent dimensional stability. Polybenzoxazines are obtained by ring opening polymerization of the corresponding monomers at elevated temperatures without catalysts and releasing by-products according to the following reaction.

They can also be polymerized by cationic initiators[5] and onium salt photoinitiators.[6] However, in these cases, the structures of the resulting polymers are complex and the properties are different than those prepared by thermal means in the absence of a catalyst. Therefore, the most of the studies on benzoxazines focused on their thermal polymerization.

Benzoxazine monomers as the polybenzoxazine precursors can be easily prepared from inexpensive raw materials like phenols, formaldehyde, and primary amines (Scheme 2).

This flexibility provides possibility of synthesizing a wide range of benzoxazine monomers with additional functionalities such as acetylene, nitrile, propargyl and maleimide groups.[7–11] The incorporation of benzoxazine groups into polymers is an alternative way to further improve the properties. The benzoxazine groups act as thermal crooslinker and while the polymer may be accountable for the flexibility of these materials. Thus, thermally crosslinked non-brittle polybenzoxazine films can be prepared. In this paper, we describe our synthetic approaches proposed to prepare benzoxazine functional polymers. The incor-

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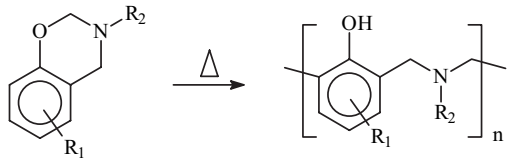

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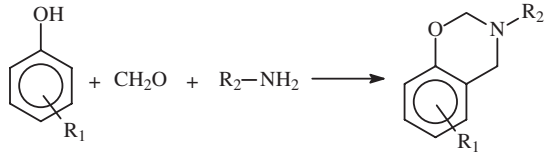
Scheme 1.
Thermal ring opening polymerization of benzoxazines.



(2)

Scheme 2.
Synthesis of benzoxazines.

poration of benzoxazine groups into polymers can proceed through two main synthetic routes (Figure 1);

- Performing polymerization of a particular monomer using a benzoxazine derivative possessing suitable initiating sites (functional initiator).
- Synthesizing benzoxazine ring structure by using a polymer with amino or phenol groups (monomer synthesis).

The shortcoming associated with the first route is the interaction of some propagating sites, i.e., cations with benzoxazine ring, particularly with nitrogen and oxygen heteroatoms. However, in some polymerization processes propagating species were unreactive towards benzoxazine and the ring structure was preserved during the polymerization. The second route is less sensitive to polymerization conditions but requires functional (mainly amino) polymers in advance. Classical monomer synthesis may successfully be followed with the available amino telechelics.

Polystyrene with Benzoxazine Group

By using Atom Transfer Radical Polymerization (ATRP), a functional end group can easily be incorporated into a linear polymer chain by varying the initiator, a low-molar-mass organic compound, RX, containing both a functional group and an activated halide. First, mono and bifunctional amino telechelics were prepared by ATRP. Subsequent application of the usual synthetic procedure involving amine, phenol and formaldehyde resulted in the formation of benzoxazine functional polystyrene.[12]

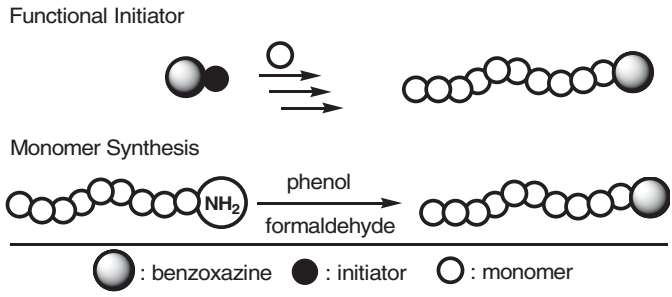
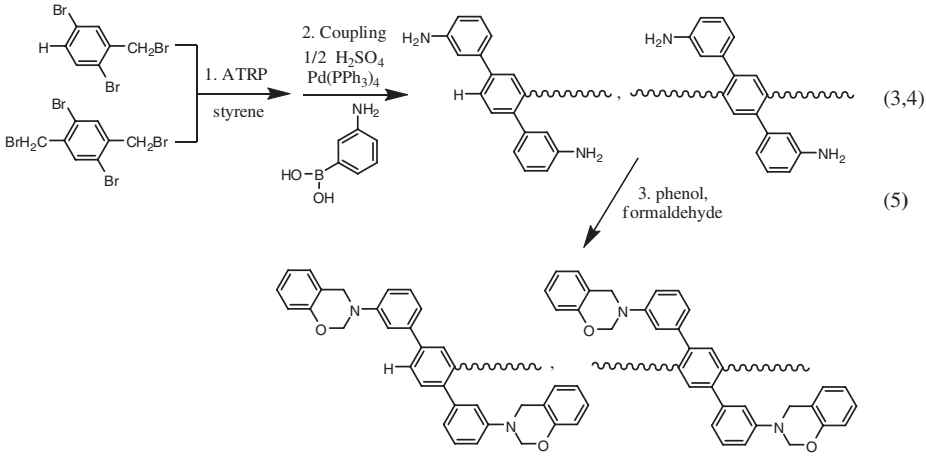


Figure 1.
Synthetic routes for the preparation of benzoxazine functional polymers.



Scheme 3.
Synthesis of mid- and end-chain benzoxazine functional polystyrene.

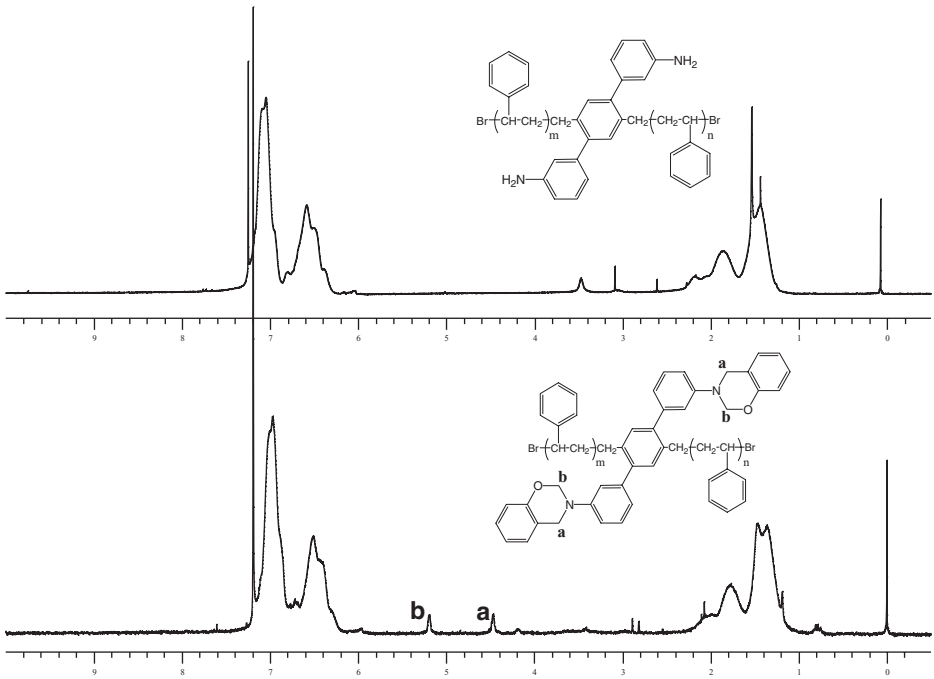
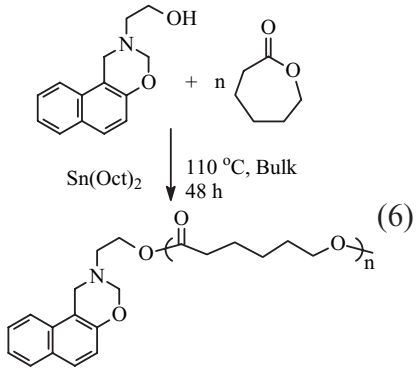


Figure 2.
^{1}H-NMR spectra of amino- and corresponding benzoxazine-functional polystyrene.

Table 1.
DSC characteristics of benzoxazine functional polystyrenes.

Polystyrene	Onset of Ring Opening (°C)	Max. Curing Temp. (°C)	Amount of Exotherm (cal/g)
Mid-chain functional	244.6	271.1	2.08
End-chain functional	231.8	258.1	1.48



Scheme 4.
Synthesis of naphthoxazine functional poly(ε-caprolactone).

Depending on the initial functionality, benzoxazine groups were located at the chain ends or mid-chains (Scheme 3). The ^{1}H-NMR spectral investigation clearly reveals the benzoxazine ring formation as presented on the example of mid-chain functional polystyrene (Figure 2).

The curing behavior of the polymers was examined by DSC. An exotherm was observed in the first run for both polymers corresponding to the ring opening polymerization in addition to the glass transition of the polystyrene segment (ca. 105 °C). The dissapearance of the exotherm in the second run was another indication for the ring opening process. Notably, polymers became insoluble after thermal treatment. The onset and maximum of curing, and the amount of exotherms were collected in Table 1. As can be seen from the table, the ring opening of benzoxazine groups located at the mid-chain of the polymer occurs at higher temperature than that of the end-chain functional one, due to the restricted mobility of the benzoxazine rings. Moreover, in the latter case, benzoxazine monomer units at the chain ends appear to be much less hindered.

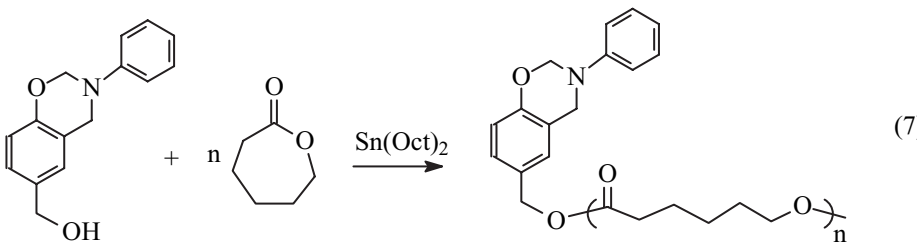
Poly(ε-caprolactone) with Naphthoxazine and Benzoxazine Groups

In view of the role of hydroxyl groups as initiators of the ring opening polymerization of ε-caprolacton (CL), the 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol was used to produce polymers containing a naphthoxazine group on one end of the chain. The synthesis of the macromonomer was performed in the presence of stannous octoate catalyst[13] (Scheme 2).

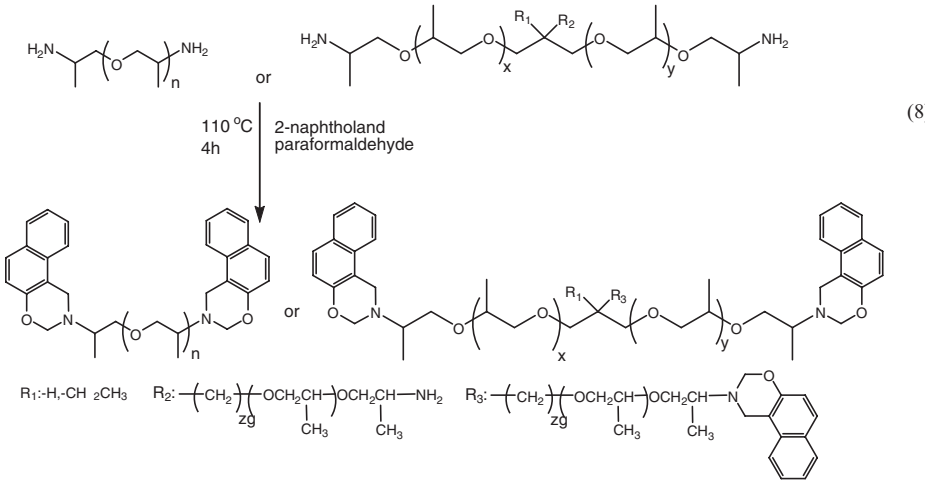
The resulting PCL macromonomer undergoes thermal cure in the presence of low molar mass benzoxazines at various temperatures with the formation of thermosets having PCL segments. Benzoxazine functional PCL was synthesized[14] by using the same strategy. In this case, the hydroxyl functionality, initiating group for the ring opening polymerization of CL, was designed on the aromatic ring of the benzoxazine.

Poly(propylene oxide) with Napthoxazine Group

As stated in the introduction section, at least in principle any polymer possessing amino groups may yield benzoxazine or naphthoxazine functional polymers. Thus, napthoxazine functional polymers were



Scheme 5.
Synthesis of benzoxazine functional poly(ε-caprolactone).



(8)

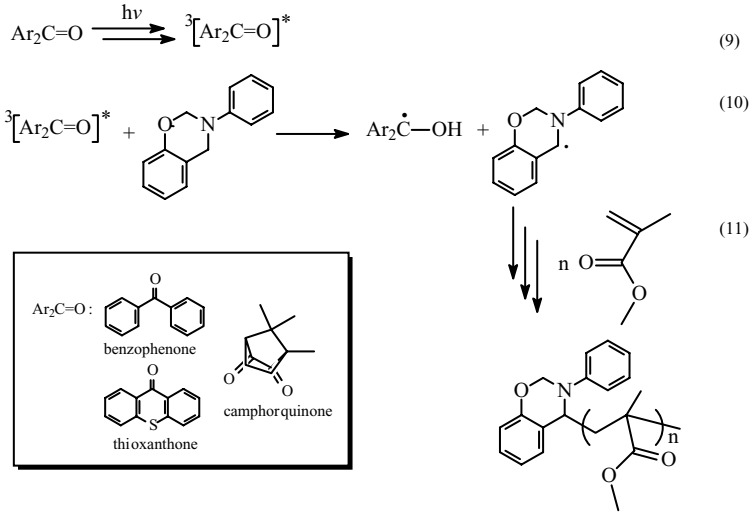
Scheme 6.
Synthesis of naphthoxazine functional poly(propylene oxide).

easily synthesized[15] by the reaction of commercially available linear (diamines) and branched (triamines) poly(propylene oxide)s (Jeffamine series) having various molecular weights, with *p*-formaldehyde, and 2-naphthol.

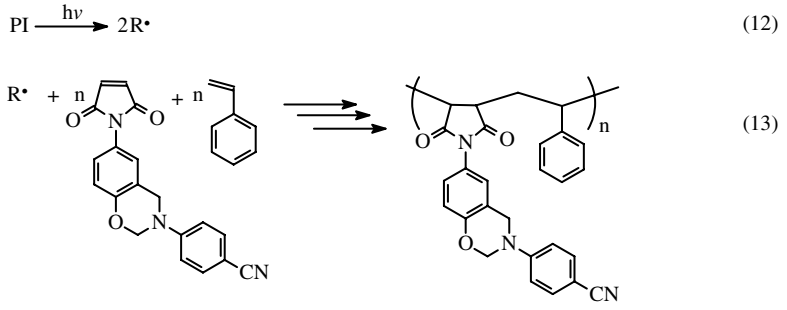
The extend of the modification (naphthoxazine formation) was strongly affected by the chain length and number of amino groups of the starting poly(propylene oxide). Curing of these poly(propylene oxide)s with classical benzoxazines resulted in the formation of networks with adjusted hydrophlicity and flexibility.

Poly(methyl methacrylate) with Benzoxazine Groups

Photoinitiated free radical polymerization can be realized by using aromatic carbonyl photosensitizers such as benzophenone and thioxanthone in the presence of hydrogen donors such as amines.[16,17] The benzoxazines possess substituted dimethyl aniline group in the structure which were recently



Scheme 7.
Synthesis of benzoxazine functional poly(methyl methacrylate) by photopolymerization.



Scheme 8.
Photoinitiated alternating copolymerization of styrene and maleimide-benzoxazine.

shown to act as hydrogen donor in photoinitiated free radical polymerization of methyl methacrylate. For this purpose, the reactions of benzoxazine with excited states of various photosensitizers was examined[18] (Scheme 7).[8]

The described photoinitiating system may be useful particularly for deep curing of thick films via a two-step procedure. During the photopolymerization, the benzoxazine ring structure was conserved and may undergo subsequent thermal ring opening reaction to yield polymers with high crosslink density. The double cure involving photo and thermal systems is expected to provide complete curing of free radical formulations which can not be achieved under normal circumstances because of oxygen inhibition and screening effect.

Poly(styrene-*alt*-maleimide) with Side-Chain Benzoxazine Groups

Photoinduced radical polymerization[19] was employed to prepare the alternating copolymers of styrene and maleimide-benzoxazine at room temperature (Scheme 8). ω,ω-Dimethoxy-ω-phenylacetophenone (DMPA) was used as photoinitiator for the polymerization. This photoinitiator absorbs light at the wavelengths where both monomers are transparent and the participation of charge transfer complex during propagation step allows formation of alternating copolymers.

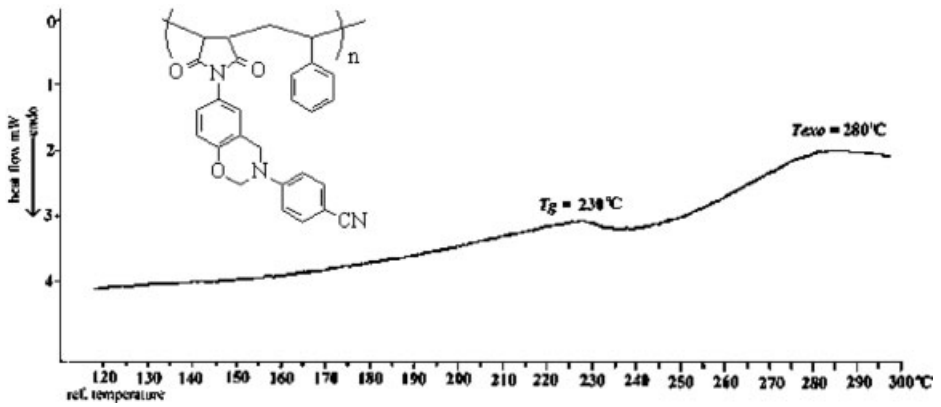


Figure 3.
DSC scan of alternating copolymer of styrene and maleimide-benzoxazine (scan rate 10 °C/min).

The thermal polymerization behavior of these copolymers was evidenced by DSC. The thermogram of a typical copolymer, having equal amount of monomer units in the composition, showed a glass transition temperature at 230 °C and an exothermic peak centered at 280 °C (Figure 3). The latter was assigned to the ring-opening polymerization of benzoxazine moieties which eventually leads to the crosslinked network.

In conclusion, it has been demonstrated that, the successful incorporation of thermally polymerizable benzoxazine into polymer chains can be achieved by using various polymerization techniques and taking advantage of the chemistry of benzoxazine synthesis. The thermal crosslinking nature provides possibility to prepare high performance thermoset polymers with diverse properties featuring both components.

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